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TRANSLATION

CONCERNING THE PROBLEM OF THE DECOMPOSITION
MECHANISM OF AMMONIUM PERCHLORATE

By

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CONCERNING THE PROBLEM OF THE DECOMPOSITION MECHANISM OF AMMONIUM PERCHLORATE

by

A.V. RAYEVSKIY and G.B. MANELIS

There is a very comprehensive literature on the thermic decomposition of ammonium perchlorate (1-9). However, sufficient attention has not been given to the problem of the development of a reaction in the single crystals of the salt. Bircumshaw (2) established, in the course of microscopic observations of partially decomposing crystals, that the process of decomposition develops at discrete nuclei. Beyond this, there were no detailed studies conducted by him. An accurate numerical study of the kinetics of the formation, size, and development of the nuclei appears to be of significant interest for the purpose of determining the reaction mechanism in the single crystals of ammonium perchlorate. In connection with this, microcinematography of the decomposition process was conducted on the single crystals of ammonium perchlorate. In addition to the microscopic observations, kinetic curves of the thermal decomposition were plotted for the single crystals, NH_4ClO_4 "in air", relative to weight loss.

The crystals NH_4ClO_4, having a dimension of 0.5 to 5mm., were grown from an aqueous solution at room temperature. The ammonium perchlorate was, first, recrystalized twice. The decomposition of the specimens was conducted in a special heating-stage, and in isothermic conditions (the temperature pre-

cision of the specimen was maintained at $\pm 1^{o}C.$). Observation and recording was accomplished with the microcamera, MKU-1.

The kinetic curves of decomposition for the single crystals, NH_4ClO_4, were plotted on a microbalance which has an automatic registration. This device was developed at a branch of the Institute of Chemical Physics of the Academy of Sciences, USSR. It has a registration precision of $\pm$ 0.05mg.

The microscopic analysis of the decomposition process of ammonium perchlorate at temperatures of 210-236^{o} (below the temperature of phase transition) showed, that decomposition reaction begins at discrete points of the crystal and develops by means of a growth of the evolving nuclei. The generation of the nucleus occurs close to the surface of the single crystal, at a depth of 20-30 microns. At sufficiently large magnifications (aprox. 1000x), it is apparent, that the nuclei of the decompositional reaction do not have a legible boundry, and consist of a large number of spherical seeds (ϕ 1-2μ). The formation and growth of the nuclei occur by means of a fusion of the seeds which originate close to the growing nucleus. Slow-motion microphotography indicated, that after generation, the seeds are in continuous motion until they fuse with the basic core of the nucleus. The seeds primarily move in a forward and backward direction, parallel to the main diagonal of the rhombus, with a velocity of 7-10μ per minute at 230^{o}. The seeds move faster when they are smaller, and they traverse a path which is hundredths of times greater than their linear size. The core gives the appearance of a static, prolated nucleus which is surrounded by a cloud of moving seeds.

Lateral to the rhombic face of the single crystal, the nuclei have a cigar-shaped form. The primary growth occurs in the direction of the main diagonal of the rhombus. The growth of the nuclei occurs at a constant speed, and takes place in a lengthwise direction ten times more often, than in a crosswise manner. (See Table 1)

① Т-ра, °С	v_1	v_2	v_3	v_4
	② μ/мин			
215	11	0,8	0,9	
220	13	1,2	1,4	
225	17	1,6	2,0	
230	25	2,4	2,9	
235	34	3,3	4,0	
250	—	—	—	5,7
255	—	—	—	6,6
260	—	—	—	8,0
265	—	—	—	9,0
272	—	—	—	11,0

Table 1. (1)=temperature. (2) = μ/minute

Note: v_1 - lengthwise speed; v_2 - crosswise speed of nuclei growth, lateral to the rhombic face; v_3 - growth rate of the nuclei, lateral to the rectangular face; v_4 - rate of nuclear growth after the phase transition.

The activation energy of the lengthwise growth is 31 ± 1 Kcal/mole; for the crosswise growth - 33 ± 1 Kcal/mole. The spread of values for the growth rate of both one and diverse crystals did not exceed 5%.

The nuclei of decomposition, lateral to the rectangular face of the crystal, are similar to a hemisphere in shape. Spallation fragments of the single crystal are produced across the nuclei of decomposition and are parallel to the rhombic face. This indicated, that only in very rare cases, a trail consisting of distinct seeds radiates from the nucleus to the depth of the crystal. The activation energy of the nuclei growth rate, which is generated at the rectangular faces, is 33 ± 1 Kcal/mole.

Figure 1 shows the growing nuclei, lateral to the rhombic and rectangular faces. Since the reaction nuclei develope anisotropicly, then the effects of the crystal habitus should be expected on the total reaction rate of the ammonium perchlorate decomposition. The kinetics of thermic decomposition for single crystals having an identical weight, but with a distinct habitus, was analysed by the gravimetric method. From figure 3, it is apparent, that the reaction rate increases with an increase of the surface segment which is presented by the rhombic facets.

In the temperature range which is higher than the temperature of phase

transition in the cubic modification of NH_4ClO_4, the decomposition proceeds across the nucleus and develops through the entire volume of the crystal. The shape of the nuclei is similar to a sphere and has clear contours. The generation occurs at a single point, whereupon, the nucleus begins to grow and develope into a fusion with adjoining nuclei. (See figure 2) The activation energy of the growth rate by the nuclei in this case is 17 ± 1 Kcal/mole.

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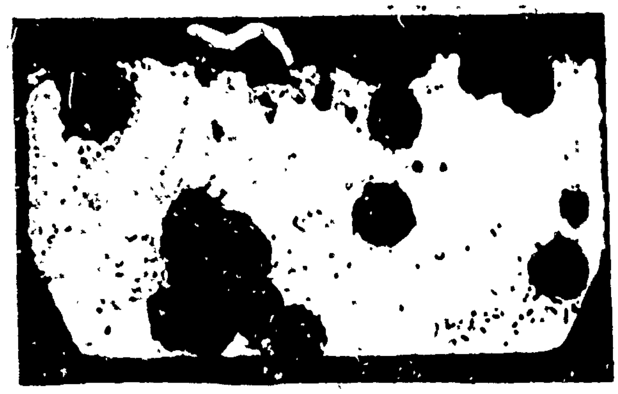

Figure 1. The Nuclei of Decomposition: a - lateral to the rhombic (300X), b - lateral to the rectangular (100X) face of the NH_4ClO_4 single crystal (t=220°)

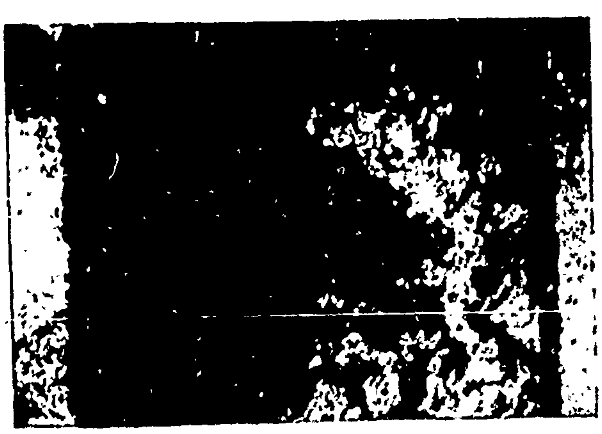

Fig. 2. View of the nuclei of decomposition (100X) in a single crystal after phase transition (t=265°)

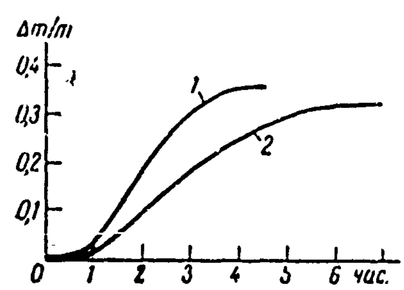

Fig. 3. Effect of the habitus on the kinetics of decomposition for the NH_4ClO_4 single crystals. The area relationships of the rhombic and rectangular facets are 2.5 : 1 for the curve 1, and are 1:1 for the curve 2.

In those cases, where the initial crystal contained a large number of growth defects, the phase transition at T=238-240° proceeded imperceptibly; cracks and strains were formed in the crystal, and a reaction developed at the defective spots which were produced.

In addition, it appeared interesting to show the characteristic features of decomposition for the single crystals of NH_4ClO_4 during the action of a catalytic agent for ammonium perchlorate, i.e., carbon (8). Micro-cinematography of the decomposition process (t=230°) for the single crystals of NH_4ClO_4 which were sprayed with a translucent film of carbon showed, that the number of nuclei significantly increases, and there is an increase of the growth rate in a transverse direction. In this case, there was no discernible variation in the mechanism of nuclear formation and growth. The experimentally observed regularities of the reaction developement in the crystals of ammonium perchlorate can be explained as deriving from the following suppositions.

In the ionic lattice of NH_4ClO_4, an electron is transfered into the zone of conductivity from an ion of ClO_4- and with the formation of a particle of $ClO_4^{\cdot}$. The electrons are partially captured at the traps with the formation of a pair of uncharged particles $[NH_4^{\cdot}] \cdot [ClO_4^{\cdot}]$. The concentration of similar types of complexes displays a thermodynamic equilibrium. A stage, kinetically limiting the reaction rate, is exhibited by the decomposition of the complex (or particles $ClO_4^{\cdot}$) with the formation of intermediate products (atoms or radicals) which are rapidly being converted into final products.

The introduction of electron donors or acceptors, and the variation, in this way, of the semiconducting properties of the crystal, increases or decreases the electron concentration in the zone of conductivity, and thereby change the balanced concentration of particles $[ClO_4^{\cdot}]$. Besides this, the number of free traps will vary, and thereby vary the concentration of complexes $[NH_4^{\cdot}] \cdot [ClO_4^{\cdot}]$. In this way, it may be possible to explain the variation of

the decomposition rate during the presence of carbon. As is known from solid state physics, the electron traps can concentrate in the vicinity of dislocations and similar types of defects. Since the dislocations are distributed in the crystal unevenly, then the reaction is generated only at definite points where the defectiveness is greater. During the reaction at distinct points, the crystal is subjected to mechanical effects due to the accumulation of products at the reaction nuclei. This leads to the emergence of strains, and as a result, to the developement of a new lattice of dislocations around the growing nucleus. Owing to the anisotropy of the mechanical properties, the dislocations develope with a primary distribution along definite axes of the crystal, which also leads to the anisotropy of the nuclear growth rate. The seeds, which were observed at temperatures below phase transition, are seemingly vesicular, and are impregnated with the products of decomposition. Their movement is probably connected with the thermal motion of the dislocations.

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